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1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE March 27, 2008	3. REPORT TYPE AND DATES COVERED Final Report, 5/1/02 - 12/31/07

4. TITLE AND SUBTITLE MURI Real Time, Explosive Specific Chemical Sensors: Spectroscopic and Time-Domain Detection of Trace Explosives in Condensed and Vapor Phases	5. FUNDING NUMBERS DAAD19-02-1-0255
6. AUTHOR(S) James B. Spicer	

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The Johns Hopkins University, 3400 North Charles St., Baltimore, MD 21218	8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211	10. SPONSORING / MONITORING AGENCY REPORT NUMBER 43569.3-CH-MUR

11. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.	12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Under this MURI, research into the use of terahertz spectroscopy, femtosecond laser-induced breakdown spectroscopy, infrared spectroscopy, laser ionization-mass spectrometry and cavity ring-down spectroscopy for explosives detection was pursued. Fundamental studies have been completed that contribute to our understanding of explosives and how they behave when being sensed using the techniques selected for study. The highest level conclusion reached in this program is that all of the techniques have the ability to detect explosives in the environment - the critical issues that are still unresolved are the ultimate selectivities and sensitivities of these techniques. At this time, it is clear that the current sensitivities of terahertz techniques allow for detection of column/surface concentrations of approximately 10 µg/cm2, laser induced breakdown spectroscopy can detect at levels below 10 µg/cm2, and cavity ring-down spectroscopy can detect vapor phase concentrations below 1 ppb. While these levels of detection have been demonstrated through work in the MURI, more important results have been obtained that point in critical directions for the success of sensing schemes that might be pursued in the future.

14. SUBJECT TERMS	15. NUMBER OF PAGES
	16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UU

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)
Prescribed by ANSI Std. 239-18
298-102

Enclosure 1

ARO MURI Final Report

Real Time, Explosive Specific Chemical Sensors

Spectroscopic and Time-Domain Detection of Trace Explosives in Condensed and Vapor Phases

Date: March 27, 2008

Prepared for:

The United States Army Research Office
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Research Triangle Park, North Carolina 27709-2211
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Contents

Executive Summary

This final report on the activities sponsored by the ARO MURI (Multidisciplinary University Research Initiative) Program under Real Time, Explosive Specific Chemical Sensors entitled "Spectroscopic and Time-Domain Detection of Trace Explosives in Condensed and Vapor Phases" summarizes the major findings obtained by the investigating team during the 2002-07 timeframe and provides recommendations for further research and development in related areas.

At the time the original program was conceived, early in 2001, the research landscape for explosives sensing and detection was vastly different from what we know today. At that time, there were only a few focused programs that sought to advance the science and technology of explosives sensing. Today, given the evolving requirements of national security tied to subsequent events, there are numerous programs supported by United States government that seek to extend our knowledge related to explosives sensing. The amount of funding allocated to these programs is formidable and significant progress in developing sensor systems has occurred. However, in the push to field systems, many fundamental issues related to explosives sensing have been overlooked. Consequently, this MURI program attempted to address a few focused questions regarding the viability and capability of various sensing technologies as they apply to explosives and explosive related compounds.

Under this MURI, research into the use of terahertz spectroscopy, femtosecond laser-induced breakdown spectroscopy, infrared spectroscopy, laser ionization – mass spectrometry and cavity ring-down spectroscopy for explosives detection was pursued. Under this program, fundamental studies have been completed that contribute to our understanding of explosives and how they behave when being sensed used the techniques selected for study in this program. The highest level conclusion reached in this program is that all of the techniques have the ability to detect explosives in the environment. At this time, it is clear that the current sensitivities of terahertz techniques allow for detection of column/surface concentrations of approximately 10 μg/cm^2, laser induced breakdown spectroscopy can detect at levels below 10 μg/cm^2, and cavity ring-down spectroscopy can detect vapor phase concentrations below 1 ppb. While these levels of detection have been demonstrated through work in the MURI, more important results have been obtained that point in critical directions for the success of sensing schemes that might be pursued in the future.

In this report, major research findings are described and directions for future research and development efforts are outlined for each of the research areas pursued under the MURI. This report was assembled using information provided by the lead investigators through program reports, presentations and discussions that took place as part of MURI interactions.

MURI Program Personnel

Many people have been instrumental in carrying out the work reported for this program. A partial listing of those involved is as follows:

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Technical Program Summaries and Recommendations

Terahertz Wave Technology for Standoff Detection of Explosives

Lead Investigators: X.-C. Zhang and Robert Osiander

When this MURI program was initiated, there were no reports regarding the spectroscopy, characterization or detection of explosives/explosive-related chemical compounds (ERCs). Commercial systems capable of performing terahertz spectroscopy measurements were starting to appear on the market, but none were capable of providing information at frequencies above a few terahertz. Consequently, a majority of this portion of the program was dedicated to generating a spectral database giving detailed information on the response of explosives at THz frequencies. Also, there was significant effort aimed at developing broadband (approximately 10 THz) terahertz systems that could be used to characterize explosives in various states.

By the end of the program, our team had characterized twenty two (22) of twenty seven (27) commonly used explosives and their related compounds documenting specific absorption signatures in the 0.5-20 THz range for all of these. We showed that signatures at low terahertz frequencies are phonon related resonances (<5 THz) and at high frequencies are single molecular resonances (>5 THz) typically associated with bond resonances. We developed various new technologies for terahertz wave generation and detection that opened new new directions for remote and high frequency terahertz testing. In particular, work at the Johns Hopkins Applied Physics Laboratory demonstrated the usefulness of novel polymer terahertz sources that were capable of providing useful terahertz emission up to 10 THz while RPI invented an entirely new concept for generating and detecting terahertz using air as a nonlinear optical medium. In addition to these important accomplishments, the team made broadly important advances that impact the use of terahertz technologies for detection of explosives in the environment.

Figure 1 shows two of the terahertz systems that were constructed to perform baseline spectroscopic measurements using time-domain, terahertz spectroscopy techniques. These techniques have been refined by various research groups over the past 15 years since they can be used to effectively gather terahertz spectra without the need for expensive and bulk cryogenic instruments. Figure 1 (a) shows a transmission system capable of generating and detecting terahertz signals up to 20 THz while Fig. 1(b) shows a reflection system that had an effective bandwidth of approximately 5 THz.

Early in the program, it was found that spectra associated with transmission measurements differed from those gathered in reflection mode. This has important implications for collection of spectra in the environment and for the comparison of these spectra to those that represent standards. In this study, spectra were gathered under conditions that are illustrated in Fig. 2(a) – namely, transmission, surface reflection from a flat surface, surface reflection from a rough surface and reflection from a surface that displays significant penetration. Under this program, it was shown that spectra gathered in transmission and reflection from flat surfaces compared favorably if tight control of
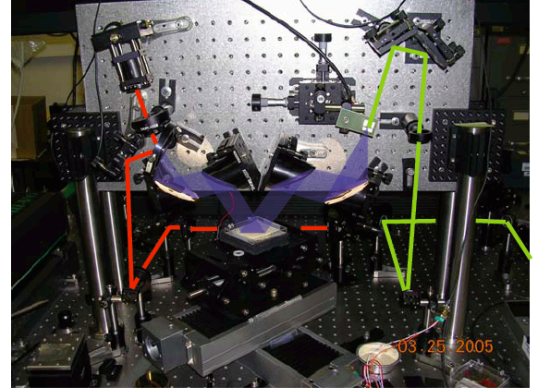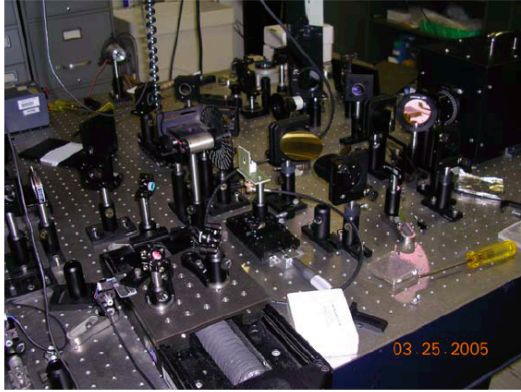
Figure 1: Time domain, terahertz spectroscopy systems configured for (a) transmission measurement and (b) reflection measurements.
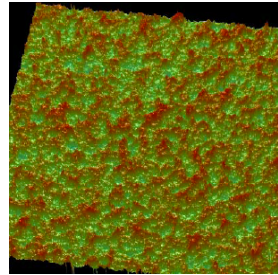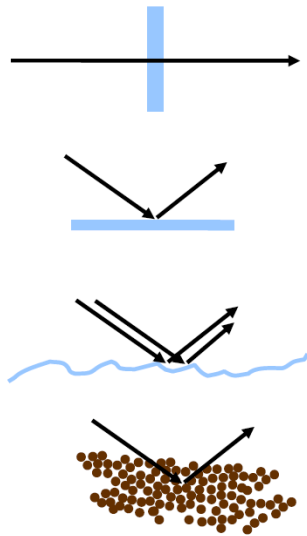

Figure 2: Sample geometries for gathering terahertz spectra. (a) Schematic representations for various interactions showing transmission through a non-scattering, transparent medium, surface reflection from a flat, surface reflection from a rough surface and reflection from a surface that displays significant terahertz penetration. These last two geometries relate to (b) where a rough, surface reflector is modeled using copper powder while soil yields a reflection that contains contributions from below the visible surface.

sample preparation process was exercised. These spectra differed significantly from spectra recorded from rough surfaces.

Using transmission measurements on explosives samples embedded in polyethylene pellets, the results shown in Figs. 3 and 4 were obtained. These figures represent typical terahertz spectra obtained for reference purposes. In Fig. 3, uncalibrated spectra for RDX, PETN, HMX and TNT are shown for frequencies up to 6 THz. Continuous curves represent measured results while vertical lines are used to mark spectral peak locations inferred using peak-finding algorithms. In Fig. 4, these spectra

were calibrated to yield absolute, terahertz, absorption cross-sections for these explosives – among all the terahertz work that has been performed on explosives, these are the only quantitative results that have been published to date. This information is critical in assessing the ultimate detection sensitivities of terahertz-based detection techniques.
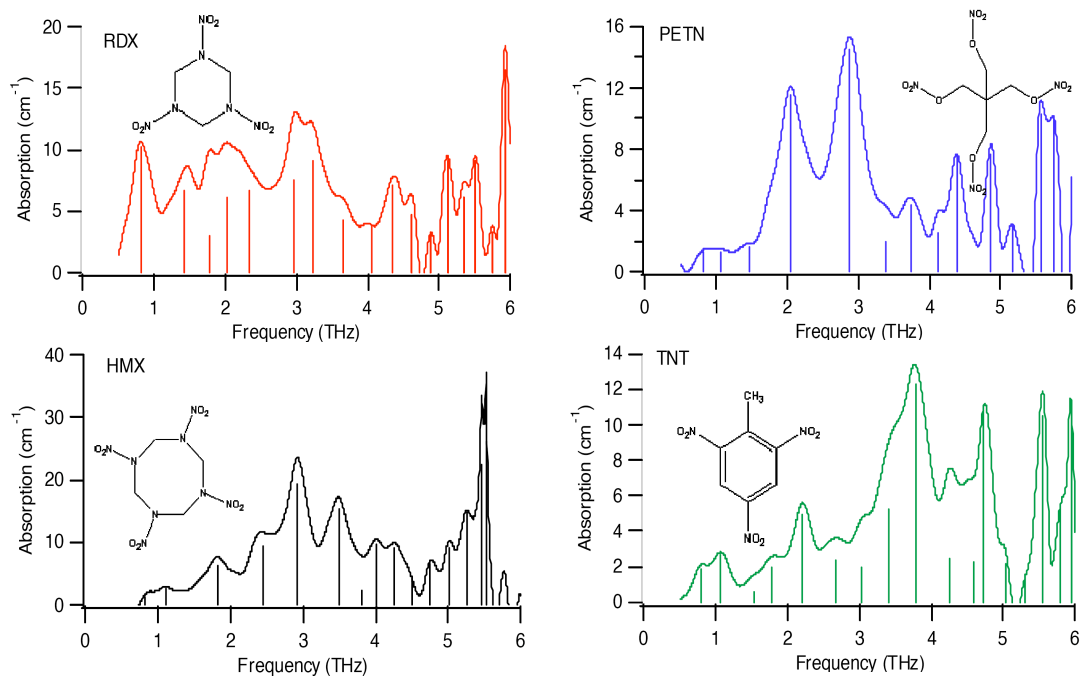

Figure 3: Broadband terahertz absorption spectra for four different explosives.
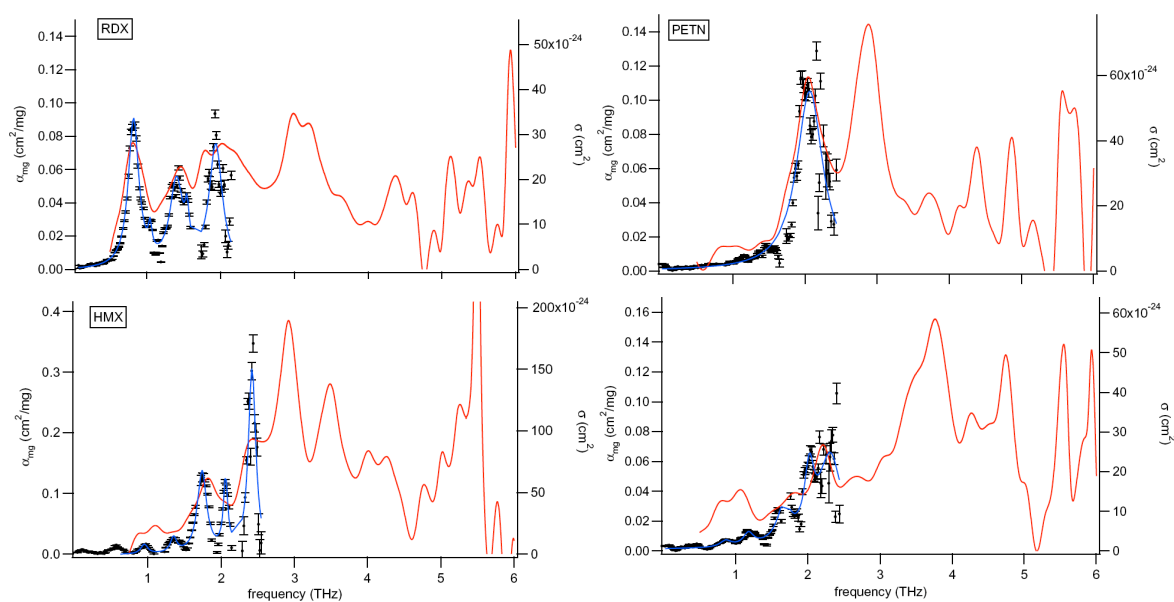

Figure 4: Absorption cross sections at terahertz frequencies for four different explosives

Under ideal conditions, the absorption spectrum for a given explosive should be independent of the experimental configuration under which it is assessed. This is true and is shown in Fig. 5 where the absorption spectrum for RDX was measured in transmission as well as in reflection at various areal densities. Overall, these spectra are quite similar and could be used to identify RDX, however it should be noted that the reflection spectra were obtained by seeding the surface of highly reflective mirror. For smooth surfaces, reflection spectra compare favorably with transmission measurements of explosives carried in non-scattering and non-absorbing matrices.
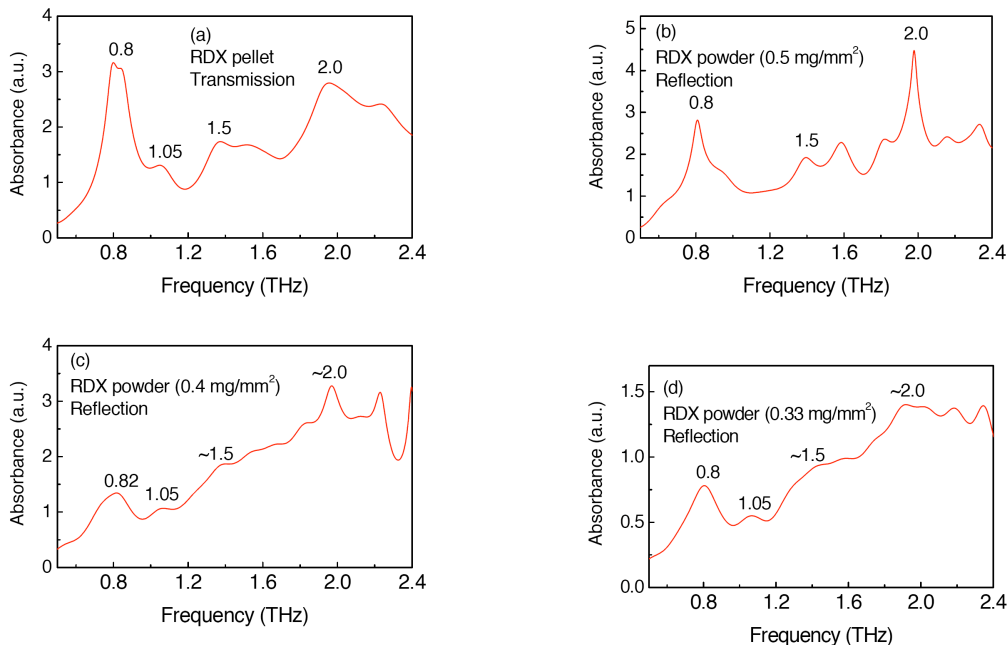

Figure 5: Terahertz absorption spectra for RDX obtained in transmission and in reflection from smooth surfaces. All spectra compare favorably and could be used to identify RDX.

Unfortunately, work under this program also demonstrated that rough surfaces rapidly degrade the quality of reflection spectra making identification of explosives on surfaces using spectrometry methods difficult. This is shown in part by the results shown in Fig. 6 where the spectral reflectivity of a copper powder surface is shown. Under ordinary conditions, copper would behave as a strong terahertz reflector and would show a constant reflectivity over the terahertz frequencies ranges used in the work under the MURI. However, if the copper is in a powdered state (yielding a rough surface), then the reflectivity of the copper becomes frequency dependent with the important result that high terahertz frequencies reflected from the surface are eliminated by coherent scattering/interference effects. In particular, the results in Fig. 6 indicate that the reflected field is more than 100 times smaller than the incident field at frequencies great than 0.5 THz. Obviously, any reflectivity changes produced by the presence of explosives at these frequencies would not be detectable.

This type of effect primarily affects the signal-to-noise of received terahertz signals and the smaller the signal-to-noise, the more difficult detection becomes. A final outcome of this program component was the determination of the signal-to-noise ratio
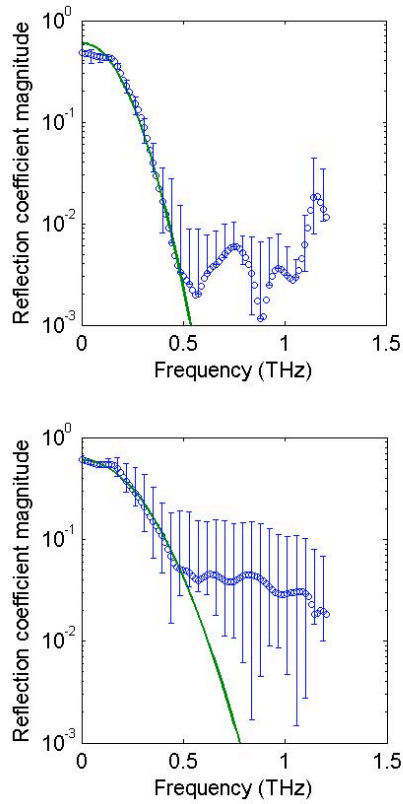
Figure 6: Spectral reflectivity of a copper powder in two states of compaction. (a) The powder surface is allowed to assume a distribution determined by gentle shaking. (b) The powder surface is tamped using a reference flat to smooth out surface variations.

required to detect explosives at given surface densities. These estimates were based on the measured absorption cross sections and are given in Fig. 7. This figure shows that the required terahertz signal-to-noise ratio must increase to detect lower areal densities of explosives and that the actual required levels depend on the absorption cross sections for explosives under consideration. In particular, it is shown that using current instrumentation under ideal conditions (yielding a signal-to-noise ratio of approximately 10,000) that the minimum detectable amount of TNT is approximately 10 μg/cm^2 (using a spectral peak at 2.3 THz). Clearly, if the TNT were on a relatively rough surface, the terahertz signal at the frequencies of interest could be a factor of 100 lower yielding a minimum detectable areal density of approximately 1 mg/cm^2.

Beyond the MURI, significant progress can be made in the area of terahertz sensing, especially as it relates to remote detection. One of the largest hurdles to overcome with regards to stand-off detection using terahertz is the presence of water
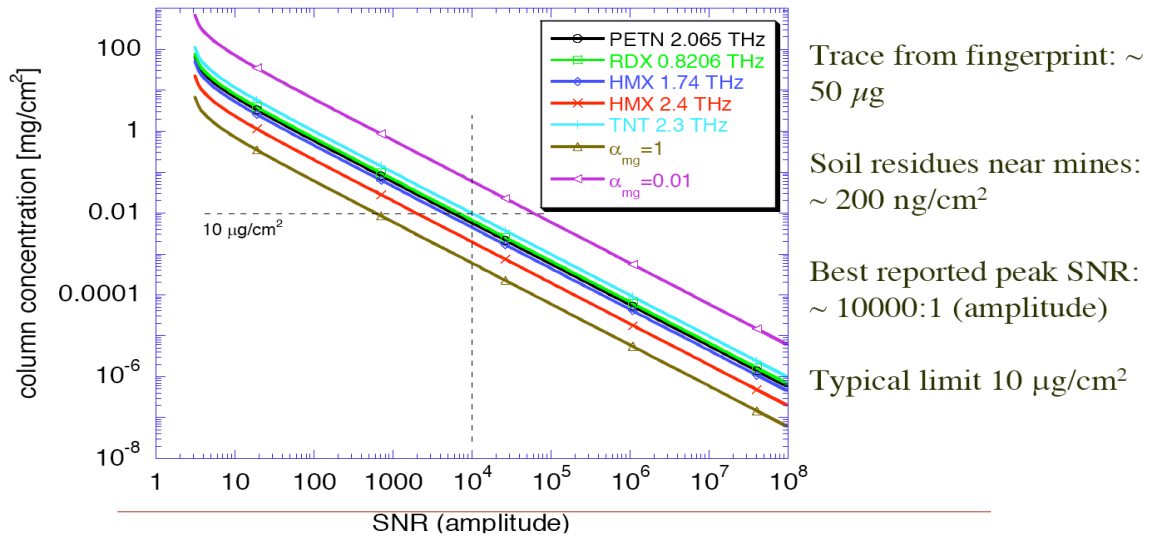

Figure 7: Estimated detection limits based on terahertz signal-to-noise ratio for various explosives.

vapor in the atmosphere – water is a strong terahertz absorber. While terahertz absorption at various frequencies can be10,000 dB greater than for visible light, new techniques developed under this MURI program have shown that terahertz can be remotely generated and detected allowing for new remote schemes for performing terahertz spectroscopy.

Current trends indicate that terahertz sources will become smaller - compact, handheld or even palm size for field application – and more efficient, meaning more terahtertz power with less electrical power consumption. Using current approaches to generating and detecting terahertz, there is every expectation that there will be a tenfold improvement in signal-to-noise ratio even as size, weight and cost are reduced..

Femtosecond Laser-Induced Breakdown Spectroscopy

Lead Investigator: James B. Spicer

Introduction

This program summary and technology assessment for femtosecond Laser-Induced Breakdown Spectroscopy (fs LIBS) is presented in three major parts:

1. An overview of LIBS technology and the estimated, ultimate capabilities of this sensor technology for trace chemical detection of explosives.

2. A review of the major accomplishments related to the fs LIBS effort.

3. An outline of future directions for LIBS technology and the challenges that remain for this sensing approach.

Overview

At the beginning of the MURI program, LIBS sensing was undergoing a renaissance within the research community. As a variant of flame/electrical discharge/plasma atomic emission spectroscopy, LIBS had been developed to a point where it was routinely used for metal alloy analysis in industrial applications however it was in its infancy as a technique for analysis of more complicated systems such as organic chemical systems – including explosives. At that time, it was well understood that a high-temperature plasma environment would yield a wide range of characteristic emission lines from excited atomic/ionic species. However unlike early LIBS investigations, our ability to measure this emission was greatly enhanced by the development of highspeed, broadbanded optical spectrometers that could effectively measure LIBS events.

As a result, many researchers began to explore LIBS using nanosecond laser pulses on a wide range of materials systems. Unfortunately, this enhanced ability to record emission spectra was not accompanied by a commensurate, quantitative understanding of the physical processes occurring in the laser excitation-emission event. It is known that laser ablation of surfaces produces a range of species in the ablation plume ranging from components of the laser-induced plasma (free electrons and ions), neutral atoms, atomic clusters and nano/microparticulate ejecta. This material removal process has been studied for many years and is only well-understood for a limited number

of systems. It is known that LIBS plasma formation on a material surface in air yields emission not only from the surface being irradiated but also from the air itself. Consequently, emission from elements common to the material and air combine to create some uncertainty regarding the origin of the emitting species. Finally, laser plume chemistry occurs yielding chemical compounds that would not exist in the absence of the excitation. Again, while these reactions are known to occur they are well-defined only for a limited number of systems.

This incomplete understanding has lead to a variety of engineering-oriented solutions to analyze and extract useful information from LIBS events. To address the incomplete conversion of ablated material into emitting atomic species, various groups have tried exciting the plume with a second laser pulse, pumping it with microwaves or confining the plume with a magnetic field. All of these approaches are essentially variants on techniques established for Inductively Coupled Plasma (ICP) spectroscopy. To compensate for emission signals related to air, schemes have been developed to analyze spectral peak height ratios. Since the composition of air is well-known, deviations in these ratios could be attributed to surface-related species. The effects of laser plume chemistry can either assist or hinder surface species identification. For example, some reactions can be tied directly back to surface species and can be used to identify these if the reactions are well understood. However, uncertainty in these reactions can often obscure the nature of the species involved in the reaction.

To date, many techniques for analysis of LIBS spectra have been borrowed from the ICP spectroscopy literature. To a great extent this has assisted in the interpretation of various LIBS spectral features including the identification of certain molecular breakdown/reaction products that result from excitation of organic molecules. However, ICP studies relate to equilibrium distributions of species in the plasma while LIBS necessarily yields significant non-equilibrium/transient contributions that can produce signatures that differ significantly from well-understood ICP results. This is true particularly for short excitation events such as occur with fs lasers. These differences open new opportunities for sensing but present largely unexplored phenomena that must be understood to perform sensing. For nanosecond duration pulses, many equilibrium features occur and can be enhanced by increasing the plasma lifetime (through pumping or continued excitation) so that LIBS results closely follow those obtained with ICP spectroscopy.

In the absence of complete quantitative understanding of the excitation-emission process, various schemes have been developed to analyze LIBS spectra of surface-borne, explosive chemical species to identify the presence of explosives versus other chemicals. These have included Principal Components Analysis (PCA) in which the large amount of data present in a LIBS spectrum is reduced to a lower dimensionality for classification purposes. For example, by examining the spectral peak height ratios for atomic species present in explosives of interest (C, N, H, O), spectra related to explosives can be separated from those of polyaromatic hydrocarbons (PAHs) or other potential. interferents. Essentially, our lack of understanding of important physical processes can be compensated using methods of signal analysis and classification. While not ideal, these methods have been successfully used with nanosecond LIBS to identify explosives and other organic compounds in laboratory tests and in field tests conducted under favorable conditions.

Stand-Off Detection and Detection Limits. Nanosecond LIBS combined with various spectral analysis procedures (including PCA) has been used to identify explosives on metal surfaces at ranges up to 50 m and has been successful in differentiating explosives from other organic compounds. No reports have been made regarding the use of LIBS to identify explosives in mixtures of chemicals that would serve as interferents in the detection process. Generally, the detection limits for LIBS have not been estimated since most published reports do not cite the areal densities for explosives that were used for analysis. Even so, estimates of detection limits are hindered by various factors including conditions for data collection, uncertainty regarding analysis algorithm performance and sample preparation procedures.

Since the excitation/plasma formation process depends on many characteristics of the system being investigated, the resulting spectral emission information depends critically on factors that might or might not have been controlled during acquisition. Research is still revealing system parameters that can optimize explosives signatures in LIBS spectra. Similarly, information extraction from spectra depends on the quality of data analysis and this directly affects detection. Some analysis procedures have been used, but these are in the early stages of development. Finally, sample preparation of explosives standards with known areal densities on various substrates is a challenge that has not been adequately addressed. While seemingly simple, our inability to deposit explosives in a controlled manner to provide known coverage on various substrates has hindered estimates of detection limits. Even with these issues, reports of TNT-on-metal spectra for1 mg/cm^2 indicate that LIBS could be pushed to 1 μg/cm^2 without too much improvement over the simplest of LIBS implementations.

Detection Rate. Owing to the irreversible changes that occur on the sample surface after LIBS analysis has been performed, there is little advantage to averaging spectra collected from the same location on a material surface. Consequently, LIBS detection can be carried out at rates dictated by spectrum acquisition and analysis – currently about 1 Hz. The rate-limiting step at this time is spectrum downloading from the optical spectrometer due to the amount of information that must be transferred from the spectrometer for analysis through standard instrument interfaces. However, decreasing the amount of spectral information that must be transferred and customizing the interface could increase detection rates to 10-100 Hz.

The projected capabilities of LIBS that should be demonstrated over the next 12-24 months are summarized as follows:

1. Level of detection in the absence of chemical interferents: 100 ng/cm^2 to 1 μg/cm^2.

2. Stand-off range for detection: 50-150 m.

3. Detection rates: 10-20 Hz.

These estimates could be improved with advances in technical approaches not detailed previously.

Accomplishments under the MURI program related to fs LIBS

At the beginning of the MURI program, no published results for LIBS of explosives existed – only preliminary ns LIBS results from ARL-WMRD were available to indicate explosives signatures. Even so, the literature indicated that the use of fs lasers for performing LIBS measurements could improve the sensitivity of the technique to surface-borne species. This is a direct result of the highly localized photothermal conversion that fs laser pulses produce resulting in an increased concentration of surface species relative to substrate/air – roughly a 1000x increase based on pulse durations. In addition, as is shown in Fig. 8, fs excitation also reduces fragmentation of the explosive molecule being sensed – this had been shown previously for vapor phase species but was one of the important findings under this MURI.

Figure 8: Schematic illustration of high energy femtosecond pulse interaction with a material surface that contains an explosive (TNT). The molecular species can be fragmented and these fragments can bond to form cluster complexes.
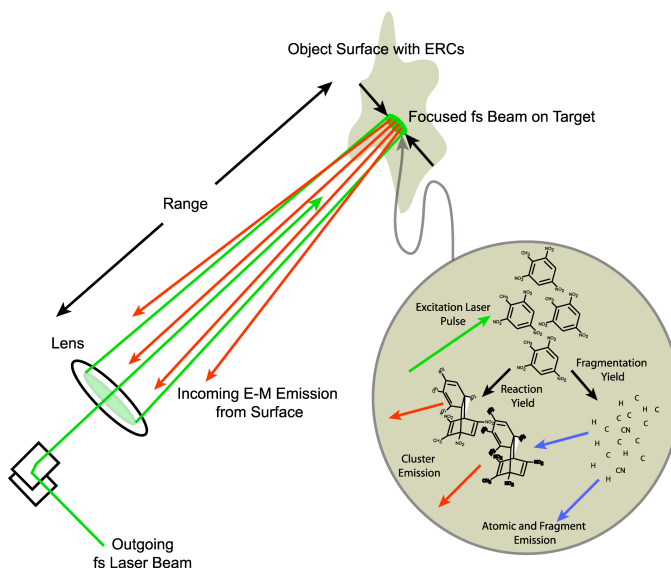
To pursue the research program in fs-LIBS pursued under this MURI, the apparatus illustrated schematically in Fig. 9 was used.
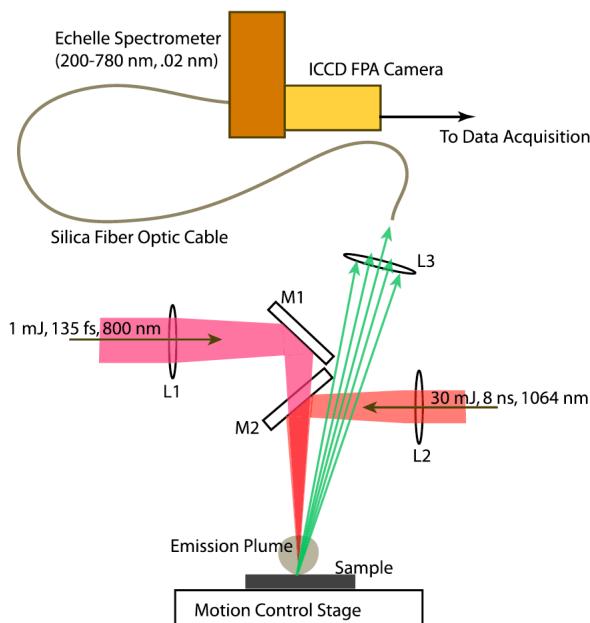
Figure 9: Experimental schematic of LIBS apparatus used for fs and ns studies of explosives on surfaces.

Not shown are the associated lasers and computer control instruments. The primary laser used for the fs studies consisted of a Ti:sapphire laser that seeded a chirped pulse amplifier yielding a 135 fs duration pulse at 800 nm with approximately 1 mJ of energy. When focused, this pulse was able to create visible emission through energetic interactions with various materials systems. For comparison purposes, nanosecond excitation was also carried out to assess the differences between fs and ns LIBS events.

Regarding these differences, we have shown that substrate and air participate to a much smaller degree in fs LIBS than in ns LIBS indicating that background in fs LIBS is smaller.

The nature of the photothermal conversion process affects the character of fs LIBS spectra. At the beginning of the program, there was no information available regarding how the laser interaction with the substrate would affect LIBS signals of surface species. Under this program, we have shown that metallic substrates produce a stronger fs LIBS signal than do non-metals owing to efficient photothermal conversion in the metal surface. In addition, we have shown that fs excitation of various explosives yield strong molecular fragment emission in the visible portion of the spectrum while ns excitation primarily yields atomic emission. This result is illustrated in Fig. 10 where LIBS spectra for TNT on aluminum are shown for both fs and ns excitation. Both spectra show substrate and contaminant-related atomic emission. However, the fs spectrum shows molecular emission related to TNT (CN and C_2) while the ns spectrum only shows atomic emission that is TNT-related (C, H, N, O).
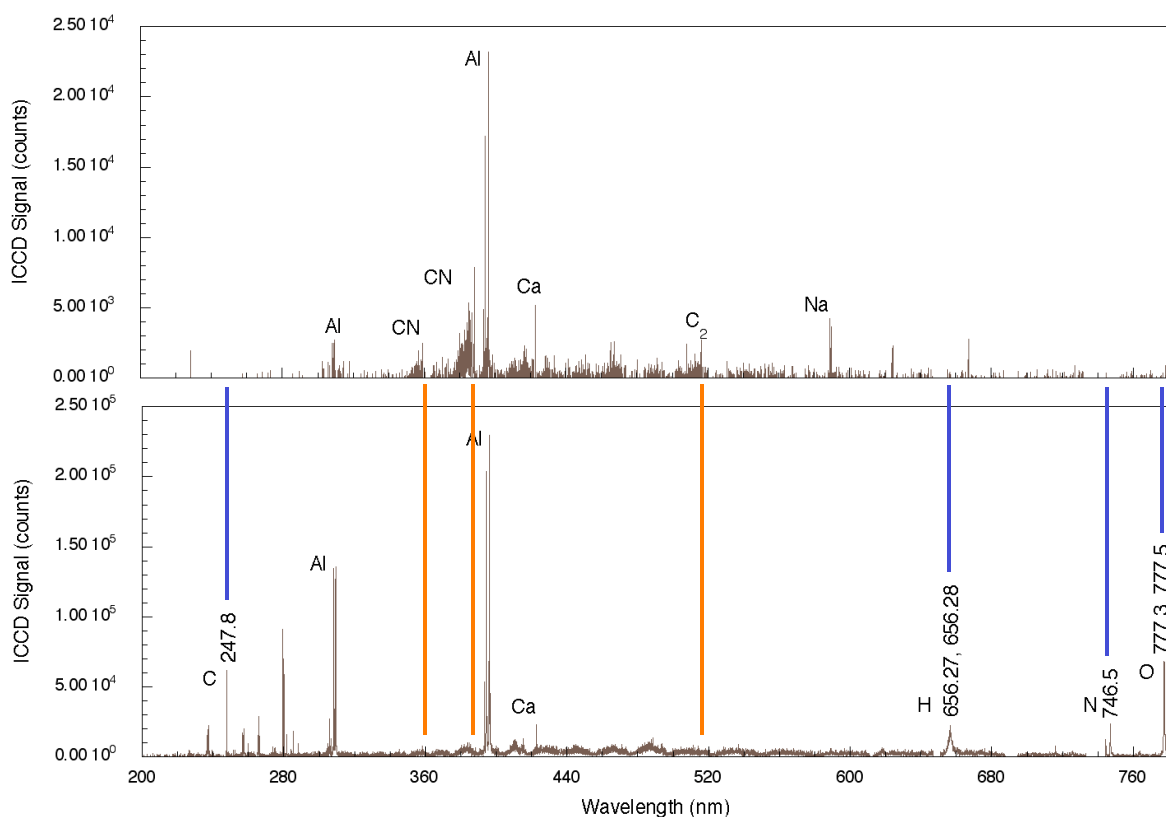
Figure 10: LIBS spectra for fs (top) and ns (bottom) excitation of TNT on aluminum. TNT-related emission is highlighted using orange lines (molecular emission in fs spectrum) and blue lines (atomic emission for ns).

Among the chemical products that result from fs LIBS of surface-borne nitro-based compounds, the emission from CN and C_2 could prove to be useful in detection algorithms. In ICP studies of PAHs, ratios of CH and C_2 have been used to identify the parent molecule. Similar approaches have been used by ns LIBS researchers who have

compared CN/C$_2$ ratios to identify parent explosive molecules. However, when performed in air, ns LIBS of organic molecules can produce both of these species. Indeed, our intial reports of CN and C$_2$ emission were met with skepticism given previous ns LIBS results. However, under this MURI, we have shown that CN formation in fs irradiated explosive samples is derived from the explosive itself or from contaminants in the explosive solution used to make samples. CN formation does not occur from the reaction of air with explosives or reactions of only air under fs excitation – this conclusion is based not only on controlled LIBS experiments but also by fs-mass spectrometry measurements that were carried out.

At the beginning of the MURI, no information existed regarding the desorption-fragmentation-ionization behavior of explosives using fs laser pulses. When fs LIBS spectra were obtained on explosives and ERCs (such as are shown in Fig. 10), they differed significantly from existing ns results – atomic emission from explosives/ERCs was nearly absent in fs LIBS spectra but was prominent in ns LIBS results. It was later determined that explosives are removed from material surfaces by fs pulses with very little decomposition into atomic constituents. Using the apparatus shown schematically in Fig. 11, we studied the desorption/fragmentation of TNT on metallic substrates and have shown that fs laser pulses for the most part do not breakdown explosive molecules to yield atomic species.
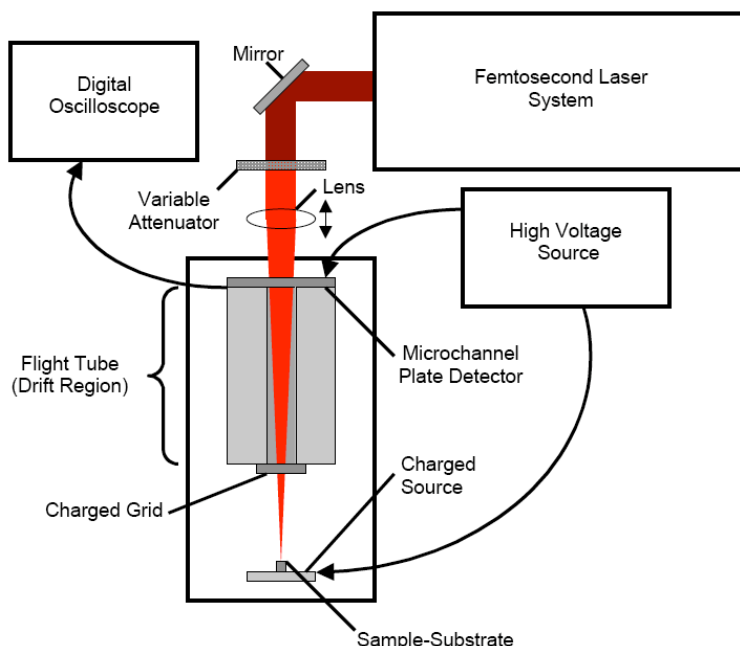
Figure 11: Experimental schematic of the femtosecond laser desorption-ionization – mass spectrometry apparatus used to study the character of species removed during excitation of TNT on metallic substates.

When LIBS fluences are used (fluences at which substrate species appear in the LIBS spectrum), explosive molecules fragment to yield large daughter species, fragments cluster to yield complexes of high molecular weight, intact molecules desorb and molecules cluster to form dimers, trimers and tetramers. This behavior explains, in part,

the differences between ns and fs LIBS. The results of this work are summarized in Table 1 where the masses of ionized species are shown as a function of fs laser pulse fluence.

TABLE 1: TNT-RELATED, ION MASS PEAKS AS A FUNCTION OF FS LASER PULSE FLUENCE

Irradiated area (mm^2)	Fluence (J/m^2)	Energy (μJ)	TNT related peaks (au)
[a]0.0056	1.4×10^5	770	227, 316, 353, 393, 408, 454, 488, 635
0.0056	1.7×10^3	10	210, 227, 322, 507, 529, 546, 571, 692
0.0056	710	4	353, 403, 507, 529, 546, 571, 677, 692, 904
1.2	500	600	136, 290, 408
1.2	420	500	136, 197, 210, 290, 408, 571
1.2	380	450	136, 299, 316, 408
1.2	180	210	None
1.2	130	150	None
1.2	42	50	None
28	31	860	121, 136, 260, 277, 400, 418, 555, 572
28	21	600	121, 136, 260, 277, 555
28	16	450	None

Work was also completed that investigated the effect of chemical isomers on recorded LIBS spectra. Figure 12 shows the fs LIBS spectra for dinitoranthranilic acid and for TNT – chemical isomers. Given the reproducibility of LIBS spectra, these results show very similar behavior for these molecules. Again, atomic emission related to the surface species is absent while both spectra show emission related to CN and to C_2. Substrate-related emission can also be clearly identified in these spectra suggesting that a significant portion of the incident pulse energy is deposited into the substrate. At this time, quantitative studies of these spectra have not been carried out and it remains to be seen if the respective spectra can be distinguished through signal classification schemes.

Understanding the effects of laser pulse interactions with the substrate is important for interpreting LIBS spectra related to detection of trace surface species. While metallic substrates do not share chemical species in common with explosives, there are broad categories of organics that share elemental constituents that are the same as are found in explosives. Essentially, substrate-related emission could mask emission from surface confined explosives or could produce a LIBS signature that appears to be similar to that of explosive. To investigate the effects of substrate on fs LIBS spectra, measurements of TNT deposited on carbon-loaded polyoxymethylene (black Delrin) were performed yielding the results shown in Fig. 13. As was the case for TNT on aluminum, there is no apparent emission related to the atomic constituents of the TNT but there are molecular emission bands related to CN and C_2. Even though the Delrin contains carbon both in the polymer molecules as well as an additive to the material, there is no evidence of emission from either of these molecules. It appears that fs excitation fragments TNT according to well-defined decomposition pathways while the polymer does not decompose in a similar fashion. This result holds promise for detection of nitro-based explosives on a variety of organic substrates.
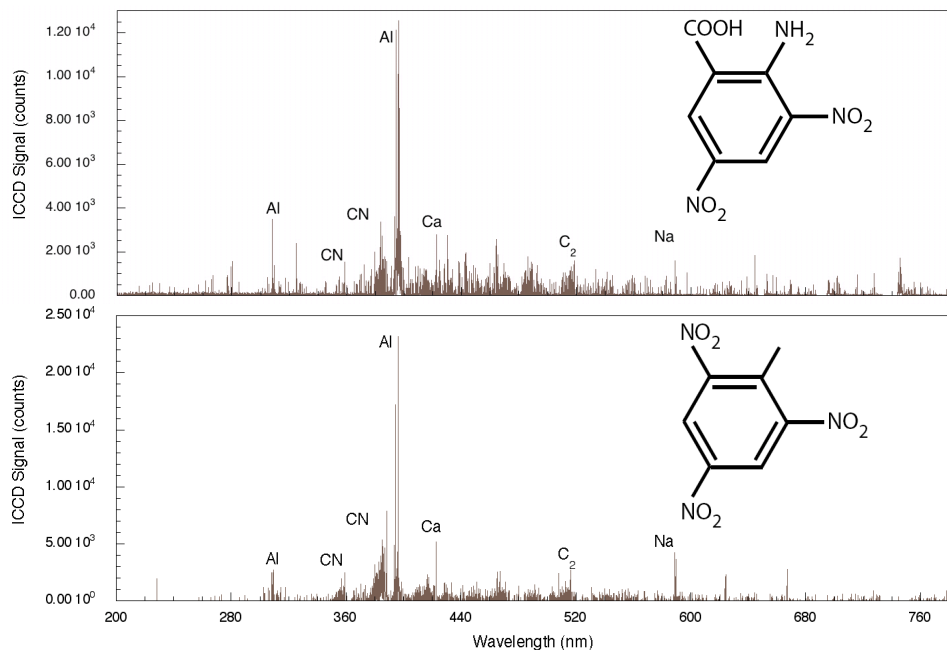
Figure 12: fs LIBS spectra of dinitroanthranilic acid (top) and of TNT (bottom) when each is deposited on an aluminum substrate.
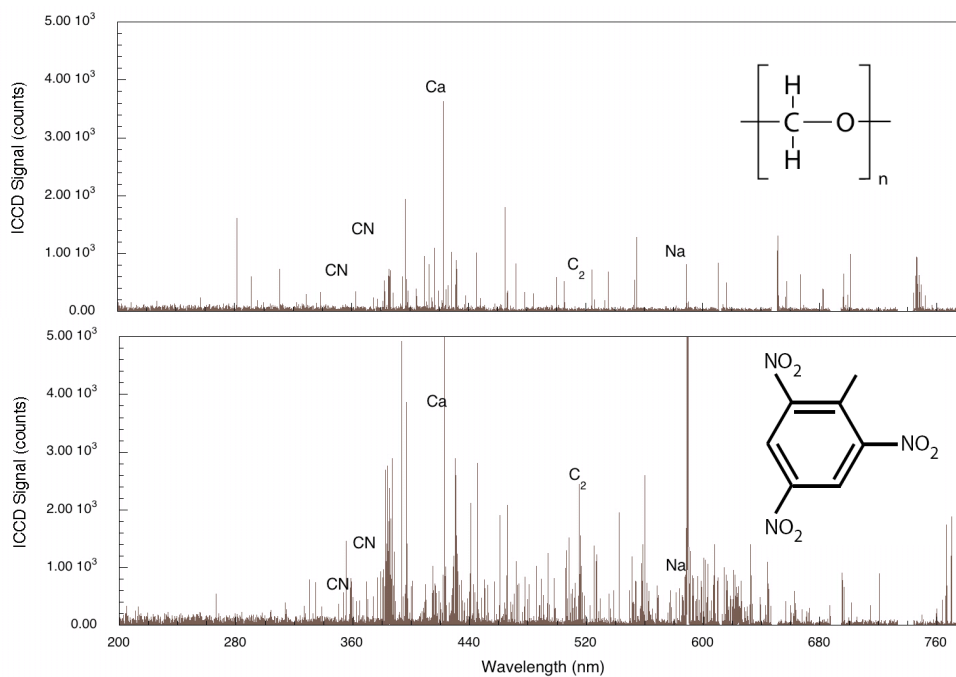

Figure 13: fs LIBS spectra of carbon-loaded polyoxymethylene (black Delrin) (top) and of TNT deposited on Delrin (bottom). Molecular emission from CN and C_2 occurs when TNT is present but is absent when a neat surface is excited.

Regarding levels of detection, we have shown that ns LIBS can be used to identify the explosives RDX and TNT on clean metal substrates at a level of 1 mg/cm^2. At this point in time, this is the only quantified areal density for LIBS detection of explosives on substrates. Related levels of detection could not be established for fs LIBS owing to instrumentation limitations in this work.

Future Directions

LIBS has various paths that need to be pursued to identify the best approaches for real-time, chemical specific sensing of explosives. For both ns and fs LIBS:

1. *Spectrum Analysis*: Chemometric analysis methods are needed that successfully extract explosive-related information from LIBS spectra.

2. *Excitation Wavelength*: Studies are needed investigating LIBS spectrum dependence on excitation laser wavelength.

The path forward for ns LIBS is fairly clear. Since the pulse duration is relatively long, the best opportunities are for pushing for complete excitation of all species in the plume to more closely match the conditions usually obtained in ICP studies.

The best directions forward for fs LIBS are not nearly so clear since many opportunities exist for significant advances in the sensing technology. Three directions are given as follows:

1. *Hyper-Spectral Emission*: Owing to the large yield of specific, explosive-related species, measurements of emission outside the visible portion of the spectrum are needed to look for signatures that unique to the explosive species. Atomic emission might not be sufficient.

2. *Pulse Shaping*: To control excitation process, fs pulse shaping can be used to enhance the yield of specific explosive-related species. This approach is related to many on-going studies in femtochemistry but no studies for explosive have been started.

3. *Plume Pumping*: Since the fs induced plume has a high density of ERCs with little substrate or air entrainment, the complete breakdown of these species after surface removal might yield a LIBS signal with better detection capabilities than current ns approaches.

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Sensitive Diode Laser Sensing Strategies

Lead Investigators: Ronald K. Hanson and Jay B. Jeffries

Optical Detection of Explosive Residues

Common explosives and explosive formulations have quite low vapor pressures, which presents both an advantage and disadvantage for detection of explosive threats. The low vapor pressure prevents the explosive residue from quickly evaporating and insures that the explosive residue has a long lifetime exposed to the atmosphere. On the other hand, the low vapor pressure provides only a small gas-phase mixing concentration above the surface of explosive residue (e.g. ranging at room temperature from 10ppb for TNT and 100ppt for RDX to an estimated seven orders of magnitude less for HMX). Thus, extreme sensitivity requirements are required for passive detection of modern explosives, and the problem (for gas-phase sensing to identify IEDe and potential suicide bombers) becomes the detection of a very weak signal in a very noisy environment.

The problem of ultra-sensitive detection has long been encountered in analytic chemistry and three detection methods have emerged for laboratory use. The first is laser-induced fluorescence; however, the extreme sensitivity needed for explosives detection is only possible for atoms and small molecules with very different electronic structure than typical energetic materials. The second is gas sampling followed by a combination of separation of chemical classes by gas chromatography followed by mass spectroscopic detection; a near-real-time variant of this approach is the jet-REMPI technique studied on this MURI by SRI as augmented by the Stanford postdoctoral researcher (to be reported by SRI). The third, pursued at Stanford and Johns Hopkins, is the use of high-sensitivity absorption methods (e.g. cavity ringdown absorption) to enhance the detection limits of optical absorption to provide the extreme sensitivity required for explosives detection. Hence our initial work was focused on the feasibility of potential explosives detection schemes for local point identification of explosive residue with eye-safe lasers in a practical environment (consistent with the detection of land mines in a relatively secure location).

Even though the land mine detection problem remains a long-term societal issue, the current DoD priorities must focus on rapid standoff detection of explosive threats with techniques that do not produce a risk to the soldier in the field or to the people or vehicles that must be interrogated as potential threats. Unfortunately, gas sampling for chemical analysis or cavity-enhanced methods for sensitive optical absorption detection are not compatible with standoff detection. In addition, potential threats must be rapidly screened for identification before they approach within the danger zone.

Standoff detection solutions might span the entire electromagnetic spectrum using a combination of X-ray, laser (UV, visible, infrared), microwave, and terahertz light sources. While recognizing that other regions of the spectrum may have advantages, we

will limit this discussion to laser-based detection methods.

Potential Solutions for Laser-Based Standoff Detection of Explosive Threats

Laser-based remote species-selective detection reduces to scattering, absorption, and fluorescence methods. The total explosive residue sample volume is too small for direct laser-based detection of the solid phase at 100m distances, and the vapor-pressure-limited concentrations are too low for passive laser-based detection. Therefore, we believe any laser-based detection scheme will require two steps: the first for stimulating enhanced vaporization (and thus augmenting the gas-phase concentration) and the second for species-selective detection of the target explosive or an identified fragment.

Laser-induced breakdown spectroscopy (LIBS) is a simple variant of this two-step approach, where the vaporization step is sufficiently energetic to produce a plasma from the laser-ablated explosive residue. The emission from the atoms and small molecules is subsequently detected and the ratio of specific emission (from specific fragments) produces the signature to identify the explosive. As the sample mass of the explosive gets smaller, the interference from the hydrocarbon-polluted atmosphere also produces breakdown emission from excited NO, CN, and the other explosive fragments, producing a false positive reading.

We propose that such tentative LIBS target identifications be followed with low-power laser ablation of the explosive residue and species-specific detection of the resulting plume. There are several alternatives for the detection step. For example, LIF of NO may prove to be a very sensitive monitor of nitrogen based explosives. Although, the atmospheric monitoring community reports that LIDAR detection of NO in the UV has much better standoff performance than LIF even though LIF has better detection limits at very short ranges; but these techniques use UV excitation which is not eye safe. In addition, NO can be made in the air plasma formed by laser breakdown, and thus has a potential interference so that it might not be the best explosive fragment to target. We believe currently that eye-safe infrared absorption (using LIDAR) is the most promising laser-based detection scheme for analysis of the laser ablation plume from explosive residue.

An improved understanding of the gas-phase plume of laser-ablated explosives is needed to understand the detection strategy because the selection of the optimum detection step will depend on the physics of the ablation step. Because there are several alternatives for the detection step, the optimization of the two-step ablation/detection scheme requires understanding of both steps. Our work on mid-IR dual-wavelength differential absorption targeted this problem, and our results illustrate that sensitive detection of specific species in aerosol-laden plumes is possible suggesting that eye-safe LIDAR may in fact be feasible to detect explosive plumes. However, it is premature to predict the detection limits until the laser-ablation plume signatures have been characterized and optimum species (or set of species) produced by laser ablation of explosives intelligently selected to unambiguously detect to identify an explosive threat.

Accomplishments under Current Program

The initial work on this project investigated the sensitivity of tunable diode laser absorption to estimate the detection limits of fixed-point explosive detection in the infrared using diode laser absorption. The demonstration experiment targeted HF direct

absorption of a transition in the first vibrational overtone band near 1.3mm. The absorption strength of the selected overtone transition is similar in magnitude to the fundamental mid-IR absorption transitions of common explosives. A minimum detectable absorbance of $6x10^{-5}$ was demonstrated, which corresponds to a detection limit of ~30ng. Thus, we estimated ~30ng absorption detection sensitivity for explosives even before the availability of mid-IR diode lasers at the proper wavelengths for explosives detection. Our laboratory feasibility study indicated that cavity-enhanced absorption techniques should be able to reduce this detection limit to ~1ng.

When the project focus moved to standoff explosives detection, we began to evaluate strategies for quantitative IR-absorption measurements in the presence of inferences from other species and aerosol scattering, as expected in the interrogation of laser-produced plumes. Toward this end, we modified a novel difference-frequency generation mid-IR laser to provide a time-multiplexed multi-wavelength output. Using this novel source we demonstrated the strong suppression of interference from aerosol scattering and interference absorption (from species with overlapped spectra) using a dual-wavelength differential absorption scheme. To our knowledge these measurements were the first differential-absorption measurements in the mid-IR using solid-state laser technology. Our preliminary laboratory results are promising and suggest that multi-wavelength mid-IR LIDAR may be feasible for detection of explosive fragments in laser-produced ablation plumes.

Laser Photoionization Detection of Explosives and Explosive Related Compounds

Lead Investigators: Harald Oser and David Crosley

Overview

The initial goal of this project was the investigation of laser photoionization techniques, coupled with time-of-flight mass spectrometry, for the measurement of explosives and explosive-related compounds (collectively referred to as ERCs). The envisioned end use of these techniques is point source detection with application to landmines. They address the chemical characteristics of the ERCs, that is, spectroscopic indentification following sampling of the ERC vapor (although sampling itself was not a project task).

Three techniques were evaluated: conventional nanosecond laser resonant multiphoton ionization (REMPI); femtosecond nonresonant multiphoton ionization (MPI); and single photon ionization (SPI). All have response times of ten seconds or less, and would thus be suitable for landmine detection for a stationary or mobile platform.

In the last year of the project, the goal of the research was altered to investigate aspects of remote, standoff detection. Specifically, we investigated a fast and efficient laser-based desorption method for tranforming low vapor pressure nitro-group-containing explosives into the gas phase for subsequent standoff detection. The emphasis was on RDX, which is an important explosive with a low vapor pressure.

Summary of Findings

ns-REMPI

This technique, which has been investigated previously elsewhere, utilizes simple, commercially available lasers and is thus easy to implement. The laser time duration is long enough (ns) to photodecompose the ERCs, so that the sole or primary ion observed is that of the NO molecule. This leads to high sensitivity, in the part per trillion level, more than adequate for all the aromatic ERCs.

However, the selectivity of REMPI is poor, as all compounds with NO_2 groups similarly decompose into NO which can be ionized. We showed that all ERCs had the same characteristic patterns, and they did not differ from ambient nitro-group-containing compounds which could be naturally present in higher concentration than the ERCs, and mask the ERC signatures.

Thus this technique is not in itself suitable for identification of ERCs at a useful level. It may serve as a "trigger device" to signal more definitive but slower methods. Moreover, it has led to a significant part of the design of a new SRI approach to stand off detection of ERCs (see below).

fs-MPI

Because the duration of this laser is in the fs regime, far less photofragmentation is observed than in REMPI, and some parent ion signal is observed. This permits indentification of the ERCs and their distinction from interfering compounds such as those naturally present. The sensitivity is in the low part per billion range, not as high as REMPI but suitable for many ERCs (such as TNT, DNT, DNB) with a high enough vapor pressure. However, at the current time, the laser technique is too complicated, delicate, and expensive to envision field deployment within the next five to ten years.

ns-SPI

This technique, also operating in the ns time regime, utilizes frequency tripling of a standard Nd:YAG laser output at 532 nm and is thus the technologically simplest method to implement. Moreover, it produces wholly or predominantly the parent molecular ion of the ERC, with no or little fragmentation. Thus it readily distinguishes among the different ERCs, and, most importantly, can discriminate against ambient interferent compounds. The sensitivity is also in the low part per billion range, and therefore suitable for field measurement.

The limitation of SPI is that, because of the laser wavelengths involved, it is limited to detection of those molecules that have an ionization potential < 10.5 eV. Fortunately, many important aromatic ERCs fall into this category. We have shown for the first time SPI spectra of nitrobenzene, o-nitrotoluene, 1,3- and 2,4-DNT, and TNT. (We do not yet know whether RDX can be ionized in this way, but will investigate in the last month of the project.)

We conclude that, for point measurements of ERCs with laser photoionization, SPI is the method of choice. This owes both to the distinction from interferents and the ease of implementation of a fieldable instrument. With suitable investment, a field prototype is ready for development.

Laser Desorption of RDX from Surfaces

In the last portion of the project, we changed the priorities to reflect the increasing interest in standoff detection of ERCs. To this end, we have studied the laser desorption of TNT and, in particular, RDX from a variety of surfaces. The detection mode is MPI, nonresonant multiphoton ionization using a fast femtosecond laser. A solid state laser beam at 532 nm desorbs the explosive, and the ionizing laser passes directly through the plume of desorbed neutrals. The geometry of this experimental configuration is shown in Fig. 14.
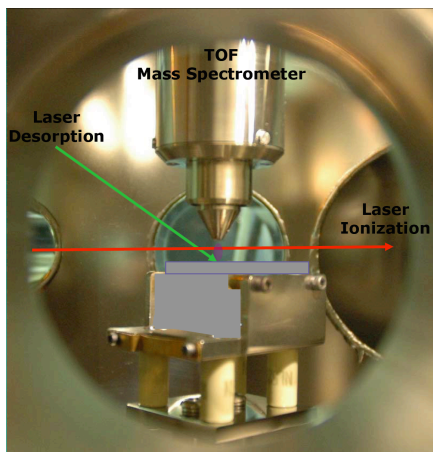

Figure 14: Photograph of the working section of the laser desorption-fs multiphoton ionization apparatus. RDX desorbed using a long-duration laser pulse is ionized using a fs pulse and is then analyzed in the time-of-flight mass spectrometer.

The key findings to date are twofold. First, we are able to desorb the explosives and detect them in quantity. This is important regarding standoff dectection of RDX which has a very low vapor pressure. Second, although the explosive does not absorb the 532 nm beam strongly, the surfaces investigated do so, heating up and assisting the explosive desorption. The influence of substrate on the desorption-ionization process was also investigated with selected results being shown in Figure 15. These results are important since they show the characteristic decomposition of RDX when it is desorbed from substrates of differing optical properties. They show the production of large, characteristic daughter fragments as well as smaller groups that could be detected using methods such as laser-induced fluorescence. This applies most primarily to the NO and NO_2 generated during decomposition of RDX – these species are known to fluoresce strongly at visible wavelengths.
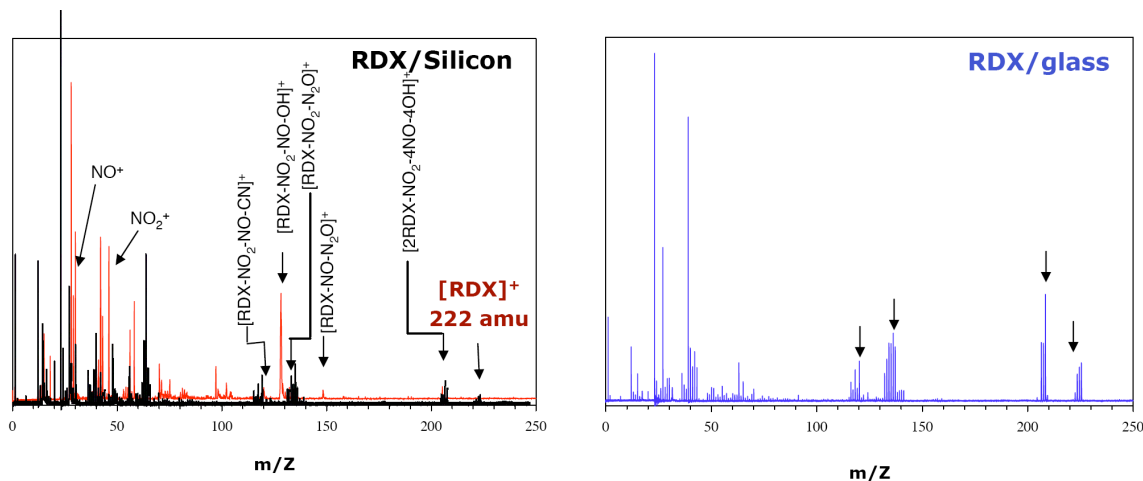

Figure 15: Laser-desorption – ionization results for RDX on silicon and RDX on glass.

Future Directions for Standoff Detection of Explosives

We feel that standoff detection of explosives can be realized using laser desorption followed by laser photofragmentation and laser-induced fluorescence of the NO fragment. Desorption of RDX from a surface can produce parts per million of the explosive, readily detectable by resonant laser-induced fluorescence. Our REMPI work shows that ambient atmospheric compounds could interfere. This would be avoided by time gating the fluorescence return signal to discriminate only for those NO molecules produced directly above the desorbing laser. Both our RDX desorption studies and signal strength calculations show that this should be a viable remote detection method.

Cavity Ring-Down Spectroscopy for the Detection of Explosives

Lead Investigator: Paul J. Dagdigian

Cavity ring-down spectroscopy (CRDS) offers a means of highly sensitive detection of vapors of explosives and explosive-related compounds (ERCs). In the CRDS technique, the sample is placed inside a high-finesse optical cavity containing the molecules of interest. The CRDS experimental configuration is shown schematically in Fig. 16. Laser pulses are injected into the cavity, and the rate of decay of the light circulating in the cavity is monitored. The absorbance of the sample is determined by comparing the photon decay rate with and without the sample in the cavity. This technique offers path lengths many times the actual sample length, and molecular concentrations are measured in a manner immune to variations of the laser pulse intensity. Another appealing characteristic of CRDS is that the absolute concentration can be determined from the absorbance with knowledge of the absorption cross section.
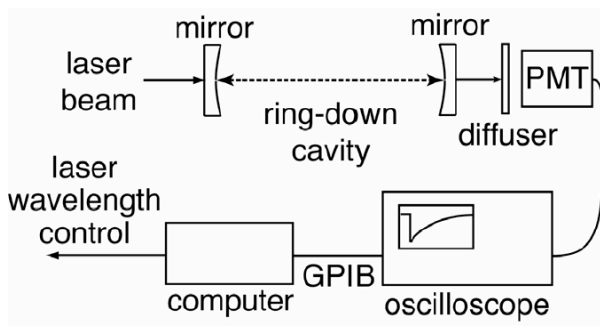

Figure 16: Cavity ring down spectroscopy experimental schematic showing the ring-down cavity into which the sample is introduced. Changes to the laser beam wavelength allow spectroscopy to be performed within limits imposed by mirror reflectivity.

The application of both UV and IR CRDS, involving electronic and vibrational transitions, respectively, to the detection of explosives has been experimentally investigated. Our laboratory has carried out a thorough study of UV CRDS for the dinitrobenzenes (DNB's) and dinitrotoluenes (DNT's) ERC's,[1] while Todd *et al.*[2] has investigated the CRDS with NO_2 stretch vibrational transitions at 6–8 μm. The nitroaromatics, including the DNB's, DNT's, and TNT have very large UV absorption

cross sections, approaching 10^{-16} cm^2 for the strong $\pi \rightarrow \pi^*$ electronic transition in these molecules. Cross sections for vibrational transitions are significantly lower, ~10^{-18} cm^2.

The detection sensitivity of CRDS, *i.e.* the minimum detectible concentration N_{min}, can be quantitatively estimated from the absorption cross section, σ_{abs}, reflectivity R of the mirrors, the fractional precision, Δ, with which the decay lifetimes can be measured, and the length l of the cavity containing the sample:

$$N_{min} = (1 - R)\ (\Delta\ /\ \sigma_{abs}\ l) \tag{1}$$

Taking $\sigma_{abs} = 8\times 10^{-17}$ cm^2 for TNT and setting $R = 99.6\%$ (typical UV reflectivity available from optics manufacturers), $l = 35$ cm, and $\Delta = 0.4\%$ (appropriate to our setup), we obtain $N_{min} = 6 \times 10^9$ molecules cm^{-3}, which corresponds to 200 ppt in 1 atm air. The room-temperature vapor pressure of TNT is ~10 ppb (see Fig. 17), so that detection of a small fraction (~2%) of the TNT saturated vapor pressure is feasible with UV CRDS. The DNB's, common impurities and decomposition products of TNT, have vapor pressures of 10–100 ppb, while the DNT vapor pressures are 200–400 ppb. The above calculation suggests that UV CRDS can detect small fractions of the room-temperature vapor pressures of these compounds, and indeed laboratory tests have achieved sub-ppb detection of these compounds.
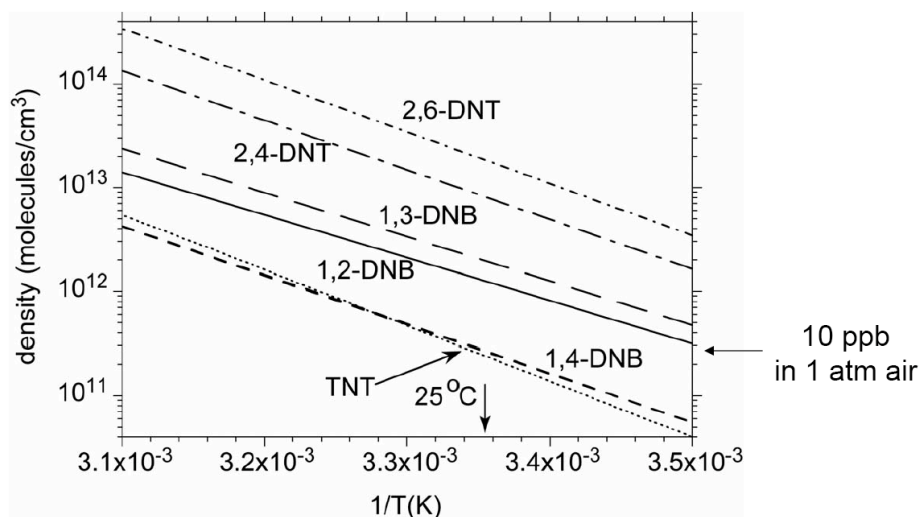

Figure 17: Equilibrium vapor concentrations for TNT and related ERCs as a function of temperature. These concentrations can be used to infer maximum TNT/ERC concentrations for comparison to expected detection sensitivities of vapor phase sensing techniques.

Measurements confirming these estimates were carried-out using the apparatus shown in Fig. 18. ERC sample dilution was controlled using nitrogen gas flow through the sample flow tube and through the bypass. Nitrogen was also passed over the cavity mirrors to prevent contamination from the vapor phase explosives sample. Results of CRDS measurements examining the measured concentration as a function of bypass flow rate are shown in Fig. 19. These results were obtained for the DNBs and show that this
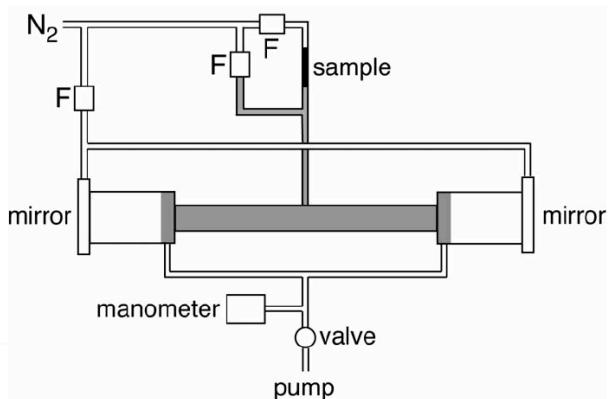
Figure 18: Cavity configuration for studying detection limits of UV-CRDS.

measurement technique can be usefully applied to sensing down to concentrations of less than a ppb – essentially the result estimated using system characteristics.

A significant limitation of UV CRDS results from the broad electronic transitions of the nitro compounds. The typical FWHM of a transition is ~40 nm. This means that singlewavelength CRDS measurements will not be able to identify the compound, and the selectivity of UV CRDS is poor. An improvement in selectivity can, in principle, be obtained through the use of simultaneous dual-wavelength detection, for example at 266 and 212 nm (4th and 5th harmonics of the Nd:YAG fundamental). However, the vapor phase absorption cross sections of these compounds are small at 266 nm, and mirrors with high reflectivities (>98%) are not available at 212 nm. It should be noted, however, that atmospheric pollutants will not interfere with the measurements, except in very highly polluted environments.

Since the photon decay lifetime is sensitive to both absorption and scattering in the cavity, we also need to be concerned about the latter in assessing the detection sensitivity. A reasonable field implementation of CRDS would involve flowing air samples at 1 atm through the optical cavity. At this pressure, there will be at ~240 nm a significant, but small (5–10%), reduction in the empty-cavity lifetime, and hence

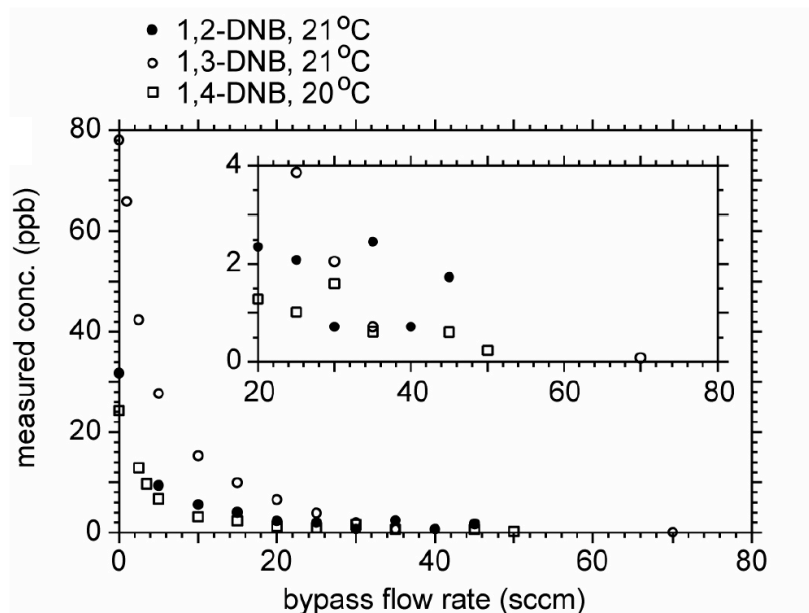

Figure 19: Measured DNB concentration as a function of the bypass flow rate. The inset shows the results at high flow rates/low concentrations and indicates that detection at concentrations lower than 1 ppb could be accomplished.

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detection sensitivity because of Rayleigh scattering. A potentially more serious problem is Mie scattering from particles entrained in the air flow. Particles will need to be removed from the flow.

An alternative approach to CRDS detection of vapors of explosives is through the use of vibrational transitions. This scheme has been investigated by Todd *et al.*[2] They have employed NO_2 bend transitions near 7 μm, which are the strongest vibrational transitions in most explosives. They demonstrate very good selectivity but significantly poorer sensitivity (by more than an order of magnitude) than UV CRDS. The lower absorption cross sections are partially compensated by the availability of higher reflectivity mirrors in the IR than the UV. The UV CRDS technique has potential application as a screening tool, in combination with less sensitive but more selective detection methods. CRDS should be considered to be a point detection sensor and cannot be readily adapted for remote detection schemes but can be used in standoff detection modality by mounting the CRDS system on a platform that can be guided to locations of interest.

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1. C. Mullen, A. Irwin, B. Pond, M. Coggiola and H. Oser,"Detection of explosives and explosive-related compounds by single photon laser ionization time-of-flight mass spectrometry," Analytical Chemistry, 78(1), 3807 (2006).
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Selected MURI Presentations
(given during final program periods)

1. R.K. Hanson (invited) and J.B. Jeffries, "Diode Laser Sensors for Ground Testing," *25ʰ AIAA Aerodynamic Measurement Technology and Ground Testing Conference*, paper 2006-3441, AIAA Washington, D.C., 2006.
2. A.E. Klingbeil, J.M. Porter, J.B. Jeffries, R.K. Hanson, "Two-wavelength mid-IR absorption sensor for simultaneous temperature and n-heptane concentration measurements," *Fifth Meeting of the US Sections of the Combustion Institute*, San Diego, March, 2007.
3. R. Osiander, "THz technologies for standoff chemical detection of explosives," UXO Countermine Range Forum, Las Vegas, Nevada, July 2006.
4. R. Osiander (invited), "Appication of THz time-domain spectroscopy in the detection of chemical agents and explosives," THz Technology Symposium, Crystal City, Virginia, May 2006.

5. R. Osiander, "Signature and signal generation aspects of exlosive detection using THz time-domain spectroscopy," International Symposium on Spectral Sensing Research, Bar Harbor, Maine, May 2006.

6. P. Dagdigian (invited), "The development of ultraviolet cavity ringdown spectroscopy for the detection of vapors of explosives and explosive-related compounds," Laser Applications to Chemical, Security, and Environmental Analysis, Optical Society of America, Lake Tahoe, Nevada, February 2006.

7. P. Dagdigian, ""Cavity ringdown spectroscopy for basic and applied studies: Investigation of polyatomic transient intermediates and detection of explosives and explosive-related compounds," JILA, University of Colorado, Boulder, Colorado, February 2006.

8. X.-C. Zhang, "THz technology and applications," Short Course, SPIE Photonic West, Jan. 23, 2006.

9. X.-C. Zhang, "New horizons of THz technology for industrial applications," Opening Tutorial Lecture, Fraunhofer Institute of Physical Measurement Techniques, 2nd International Forum on THz Technology, the Technical University of Kaiserslautern, Germany, March 1,2006.

10. X.-C. Zhang, "Recent development of THz wave sensing, imaging science, technology, and applications," APS March Meeting, Baltimore, March 15, 2006.

11. X.-C. Zhang, "THz wave emission microscope," Government Microcircuits Applications & Critical Technology Conference (GoMacTech-06), Tutorial Series of THz-Frequency Sensing for the Future, Paradise Point Resort, San Diego, March 20, 2006.

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13. X.-C. Zhang, "THz wave imaging," Frontiers in Imaging, International Congress of Imaging Science 2006, Rochester, NY, May 11, 2006.

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19. Y. Dikmelik, C. McEnnis and J. Spicer, "Femtosecond laser-induced breakdown spectroscopy of explosives," JUXOCO 9th Annual Army Landmine/UXO/IED Basic Research Technical Review Meeting, February 2006.

20. James B. Spicer: "Energetic Chemical Species Detection using Terahertz-Based Spectroscopy Technologies" Lawrence Livermore National Laboratory. August 24, 2006. (Invited)

21. Y. Dikmelik, C. McEnnnis, and J.B. Spicer: "Femtosecond Laser Induced

Breakdown Spectroscopy of Explosives" SPIE Defense and Security Symposium. Orlando, Florida. April, 2006.

22. C. McEnnis, Y. Dikmelik, and J.B. Spicer: "Investigation of Explosives Fragmentation by Femtosecond Laser Mass Spectrometry" SPIE Defense and Security Symposium. Orlando, Florida. April, 2006.

23. James B. Spicer: "Laser-Induced Breakdown Spectroscopy: Energetic Optical Interactions with Surface-Borne Explosive-Related Compounds" Army Research Laboratory NVESD NVL. March 19, 2006.